



A review of membrane technology for bioethanol production



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ABSTRACT

Bio-ethanol as a clean and renewable fuel has gained more attention; however greater energy inputs make a slow progress in industry. Membrane technology has potential in the bioethanol production process as a highly selective and energy-saving separation process. This review presented membrane technologies applied in three aspects: (i) microalgae harvesting, (ii) sugar concentration and detoxification, (iii) bioethanol recovery. The performance of different membrane processes was summarized and compared. The advantages and limitations of membrane technologies for these applications are discussed, and it was thought that the hybrid process has great potential in improving membrane efficiency.

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1. Introduction

The increasing energy crisis and growing environmental concerns in recent years have driven the development of technologies to allow for the substitution of fossil fuels with renewable energy [1–4]. Several alternatives are currently being explored, including a range of carbon-free and renewable sources (photovoltaics, wind and nuclear power, hydrogen) in an attempt to replace natural gas, coal and oil in the electricity generation sector. However, there is no such equivalent in transportation, since fuel cells, electric/

hybrids and natural gas-based cars are still a long way from becoming mainstream vehicles [5].

Bio-ethanol as a clean and renewable fuel has gained more attention. It can be produced from all kinds of renewable materials such as corn, sorghum, cellulose and algae biomass. On the basis of the raw material used for its production, bioethanol is divided into first-, second- and third-generation bioethanol [1]. The classification of bioethanol is shown in Fig. 1. Burning ethanol instead of gasoline reduces global warming emissions of 20% from corn ethanol and 85% from cellulosic ethanol while entirely eliminating the release of acid rain-causing sulfur dioxide [6]. Meanwhile, bio-ethanol can be added to gasoline for transportation which has been applied in several countries. In Brazil, more than 15% of cars can run on pure ethanol [7,8]. However, bio-ethanol production involves many processes such

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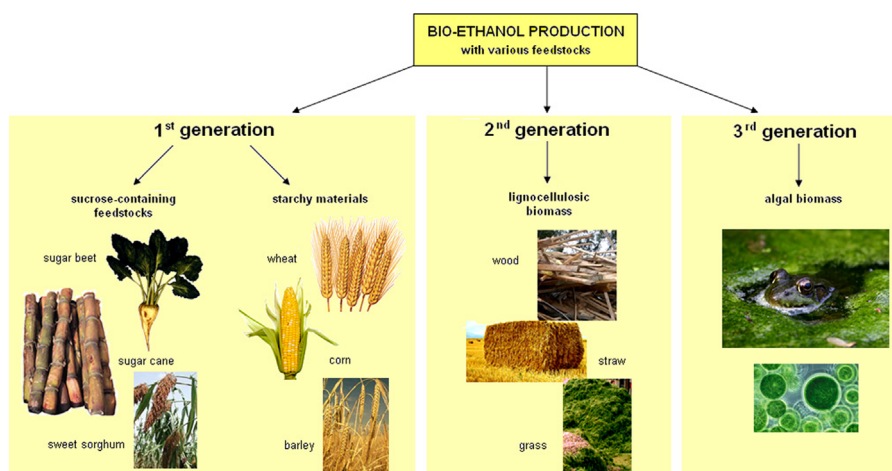


Fig. 1. Classification of bioethanol [17].

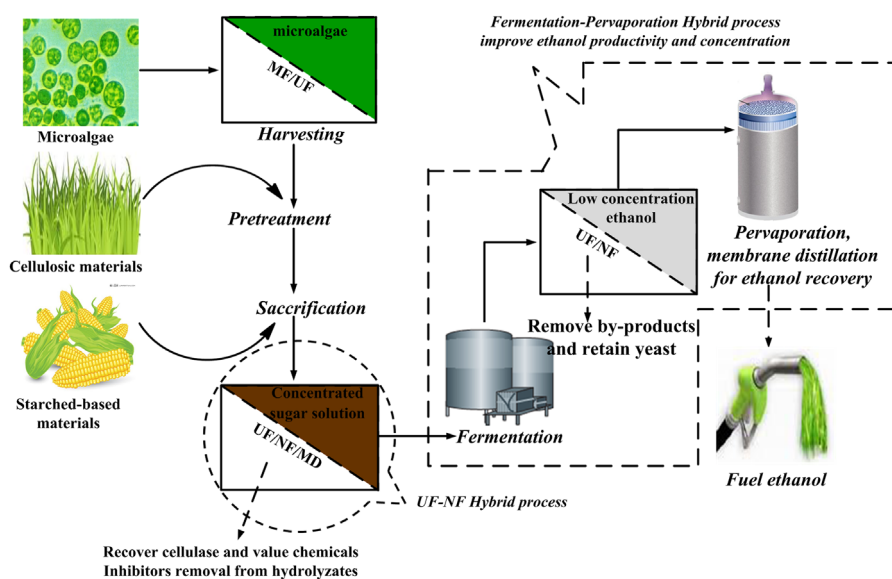


Fig. 2. Application of membrane processes for three generations of bioethanol production.

as pretreatment, fermentation, recovery and the refining process [9]. A total of 5.99 kJ of fossil energy is expended to produce 4.19 kJ of ethanol. The largest energy inputs in corn-ethanol production are for the steam and electricity used in the fermentation/distillation process [10]. Bioethanol will not be significant without improvements in this process and reduced energy requirements. Membrane separation technologies have gained more and more attention due to their reduced energy requirements, lower labor costs, lower floor space requirements and wide flexibility of operation [11]. This technology has applied in many processes of bioethanol production instead of the traditional process [12–16]. The aim of this article is to present a state-of-the-art review on the applications of membrane technologies for bioethanol production such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), membrane distillation (MD) and pervaporation (PV). We also discuss the problems confronted with every membrane process.

2. Membrane technology applied in bioethanol production

An overview of ethanol production with potential membrane applications is depicted in Fig. 2. The first potential membrane application is the harvesting of microalgae for third generation

bioethanol synthesis. By the use of MF/UF, it is possible to recover microalgae. For second and third generation bioethanol, pretreatment is a necessary step to make the carbohydrates in the biomass accessible for conversion. The second potential membrane application is the purification and concentration of prehydrolyzates after pretreatment and before fermentation. MD, NF and RO can concentrate the sugar solution and remove inhibitors to fermentation. Regarding recovering the enzyme and other value-added production, an NF process has been considered, combined with UF. After fermentation, low concentration bioethanol is sent for pervaporation and pre-concentration. Fermentation and pervaporation have been integrated in order to perform continuous fermentation. During the hybrid process, UF and NF can be used to remove fermentation inhibitors and yeast. The section part will provide a detailed introduction for each membrane process.

3. Membrane technology for microalgae harvesting

Microalgae is getting more and more attention as a raw material for bioethanol production as it provides carbohydrates and proteins that can be used as carbon sources for fermentation. Meanwhile, microalgae cells have a very short harvesting cycle

(1–10 days) compared with other feedstocks (harvest once or twice a year) and thus provide enough supplies to meet ethanol production demands. On the other hand, algal biomass avoids the issues met with first- and second- generation bioethanol, namely food–fuel competition and land-use change [18].

However, algal biomass harvesting is a challenge because of the small size of algal cells (3–30 μm in diameter), their similar density to water and the large volumes of water that must be handled to recover the biomass. Recovery of the biomass from the broth has been claimed to contribute 20–30% of the total cost of producing the biomass [19]. Therefore, a suitable harvesting technology is very important for bioethanol production using algal biomass. Generally, microalgae harvesting can be undertaken by the technologies as shown in Table 1. As can be seen, membrane filtration is known to be not energy intensive compared to other methods, as this technology is isothermal and involves no phase change. Meanwhile, it offers the advantages of almost complete retention of biomass as well as potential disinfection via the removal of protozoa and viruses [20,21]. Furthermore, no chemicals such as coagulants or flocculants are required, thus preventing their accumulation in the biomass or the recycling streams that exist in a coagulation–flocculation process [22]. Especially for smaller algae cells (< 30 μm), membrane filtration is a technically viable alternative to conventional filtration. Membrane filtration applied in microalgae harvesting was first reported in 1995. Petrusevski et al. [23] investigated the capability of a tangential flow filtration (TFF) system, equipped with a 0.45 μm pore-size membrane to concentrate algae from large volumes of reservoir water. An overall algal biomass recovery of 70–89% was found. Although membrane filtration has many advantages compared to other technologies, studies have found that membrane fouling will be severe under some operational conditions. Therefore, it is very important to choose the proper membrane material and operation model for membrane filtration.

3.1. Membrane material for microalgae harvesting

Micro- and ultrafiltration have been proven to be effective to harvest microalgae. Membranes prepared from different materials could provide variable harvesting performance, but there is no criterion regarding the membrane material for microalgae harvesting. Rossi et al. has performed studies on membrane materials

for microalgae harvesting [33–35]. They investigated 11 commercial polymeric membranes for harvesting the cyanobacterium *Arthrospira platensis* by cross-flow MF and UF techniques. Hydrophilic membranes seemed more efficient than the others in terms of steady-state permeation flux. Furthermore, such membranes were easier to clean, partly because the negative charge decreased membrane fouling and cake formation, which represent the majority of the total resistance; this can be removed by a single rinsing step. In addition, they evaluated 14 inorganic membranes for the separation of *Arthrospira platensis* from a diluted culture medium. The UF membrane ATZ-50kD exhibited the best permeation flux and cleanability.

According to the above studies, it can be concluded that hydrophilic organic and inorganic UF membranes are more suitable to microalgae harvesting.

3.2. Membrane fouling

Although membrane filtration is a better technology for microalgae harvesting, the flux will decline due to membrane fouling, which limits the large-scale application of membrane technology. Therefore, understanding membrane fouling by the biomass and developing anti-fouling strategies are critically important for sustainable biomass concentration using membrane technology. However, only a few reports on the algae/water separation process have described the fouling of membranes and solutions to mitigate fouling [36–40]. Membrane fouling is mainly caused by bacteria, algae, inorganic colloids and organic material such as proteins and polysaccharides. On the other hand, several studies have developed potential options for membrane fouling control. There are different techniques to limit the fouling phenomenon, among which are the use of the proper membrane material and altered operation conditions. Available membrane materials have been summarized in Section 3.1.

The enhancement of membrane shear-rates has long been recognized as one of the most efficient factors for fouling control. Increasing the cross-flow velocity decreases membrane fouling [38]. Thus, controlled hydrodynamic conditions, such as a low TMP and low shear rate, are required in order to limit fouling and cell damage [41–44]. Rios et al. [45] used a rotational-dynamic filtration system to harvest *Phaeodactylum tricornutum* microalgae. They studied the effect of rotational speeds and TMP on membrane

Table 1
Description of microalgae harvesting technologies.

Process	Description	Solids concentration after harvesting [24]	Recovery [24]	Chemicals	Energy usage	Limitations
Coagulation/flocculation	Based on the microalgae cells that carry a negative charge	—	66–98%	Yes	Low energy requirement for slow mixing; varies largely	Only as preparatory step prior; Flocculants is expensive at high dose [25]
Flotation	Based on the trapping of algae cells using dispersed micro-air bubbles [26]	3–6%	50–90%	Yes	High dissolved air flotation 10–20 kWh/m ³ [27]	Limited evidence of its technical or economic viability [28]
Gravity sedimentation	Based on Stoke's law [29]	0.5–3%	10–90%	No	Very high 8 kWh/m ³ [30]	Only suitable for large (ca. > 70 μm) microalgae [31]
Centrifugal	Based on Stoke's law [29]	12–22%	> 90%	No	Energy intensive	High energy costs higher maintenance requirements [32]
Membrane filtration	Based on molecule size	5–27%	90–100%	No	0.4 kWh/m ³	Membrane fouling
Electrophoresis techniques	Based on microalgae able to behave as colloid particles	Depends on the process	Varies	Yes	Varies	Electrodes need to be replaced periodically

Table 2

Summary of the membrane process applied in sugar concentration and inhibitors removal.

Inhibitors/ sugar	Membrane process ^a	Separation mechanism	Scale ^b	Driven force	Membrane		Operation conditions ^e			Flux (L m ⁻² h ⁻¹)	Rejection (%)	Disadvantages	Advantages	Reference
					Material ^c	Configuration ^d	pH	T (°C)	P (bar)					
Sucrose	VMD	Relative volatility	L	Vapor pressure difference	PP	T	–	40	0.0067	0.45	> 98%	Low flux and no special membrane material	Utilize low low-level heat	[60]
Sugar	VMD		L	Vapor pressure difference	PVDF	F		65	–	8.46	99.5			[63]
Glucose	NF	Size exclusion	L	Pressure	Proprietary	F	2.9	25	24.5	120.8	100	Membrane fouling	High rejection and high flux	[51]
Glucose	NF		L	Pressure	PVA	–	–	30	13.78	15	99			[68]
Glucose	NF		L	Pressure	PVA	–	5.6	50	17.5	60	99			[64]
Glucose	NF		L	Pressure	PA	–	10	25	13	26.5	99.2			[67]
Glucose	NF		L	Pressure	PA	–	3	25	11.5	39.8	95			[67]
Xylose	NF		L	Pressure	Proprietary	F	2.9	25	24.5	120.8	96.4			[51]
Xylose	NF		P	Pressure	PA	F	–	28–30	20	24	99.1			[56]
Xylose	NF		P	Pressure	CTA	F	–	28–30	20	32	66.7			[56]
Xylose	NF		L	Pressure	PA	–	10	25	13	26.5	99.5			[67]
Xylose	NF		L	Pressure	PA	–	3	25	11.5	39.8	86.8			[67]
Xylose	NF	Size exclusion and solution-diffusion	P	Pressure	Proprietary	S	2.9	25	24.5	–	85	The rejection depends on pH	Low energy consumption High flux	[71]
Xylose	RO		L	Pressure	PA	P	2.93	25	20	23.62	99.67			[74]
Glucose	RO		L	Pressure	PA	P	2.93	25	20	23.62	99.78			[74]
Glucose	RO		L	Pressure	Aromatic	–	2	21	25	–	48			[75]
Glucose	RO		L	Pressure	Aromatic polyamide	–	2	21	25	–	82			[75]
Acetate	NF	Donnan effect	L	Pressure	PVA	–	–	30	13.78	15	60	The rejection depends on pH	Low energy consumption High flux	[68]
Acetic acid	NF		L	Pressure	Proprietary	F	2.9	25	24.5/34.3	120.8/142.4	– 19.0 – – 14.9/ – 31.8 – – 27.7			[51]
Acetic acid	NF		P	Pressure	Proprietary	S	9.1		24.5		90			[71]
Acetate	NF		L	Pressure	PVA	–	5.6	50	17.5	60	40			[64]
Acetic acid	RO		L	Pressure	PA	P	2.93	25	20	23.62	52.53			[74]
Acetic acid	RO		L	Pressure	PA	P	9.88	25	20	–	99.28			[74]
Acetic acid	RO		L	Pressure	CA	–	2	21	25	–	25			[75]
Acetic acid	RO		L	Pressure	CA	–	2	21	25	–	– 5			[75]
Furfural	VMD		L	Vapor pressure difference	PVDF	F	4.53	70		6.42	100			[63]
Furfural	NF		L	Pressure	PA	–	10	25	13	26.5	31.8			[67]

Table 2 (continued)

Inhibitors/ sugar	Membrane process ^a	Separation mechanism	Scale ^b	Driven force	Membrane	Operation conditions ^c	Flux (L m ⁻² h ⁻¹)	Rejection (%)	Disadvantages	Advantages	Reference
Furfural	NF		L	Pressure	PA	3	11.5	3.6			[67]
Furfural	NF		L	Pressure	Proprietary	2.9	25	120.8/142.4			[51]
Furfural	RO		L	Pressure	PA	-	28	50			[77]
Phenols	RO		L	Pressure	PA	-	28	> 80			[77]
Acetone	RO		L	Pressure	PA	-	28	> 80			[77]

^a VMD= vacuum membrane distillation, NF= nanofiltration, RO= reverse osmosis.^b L= laboratory; P= pilot scale.^c PVDF= poly(vinylidene fluoride), PP= polypropylene, PVA= polyvinylalcohol, PA= polyamide, CTA= cellulose triacetate.^d F= flat, P= plate, S= spiral wound, T= tubular.^e T= temperature, P= pressure.

fouling. As the speed increased, the flux increased due to reduced membrane fouling caused by concentration polarization. Meanwhile, it can be stated that fouling effects which reduce the permeability of the membrane increase when the TMP also increases. Zhang et al. [46] developed an efficient technology for harvesting of algal biomass using membrane filtration and established anti-fouling strategies. Air-assisted backwash with an air scour and higher cross-flow velocity can control membrane fouling. Bilad et al. [47] developed a method to harvesting microalgal biomass using submerged MF membranes. They used an improved flux-step method (IFM) to characterize the membrane fouling. The IFM results suggested lower degrees of fouling compared to conventional submerged MBRs within the range of operational parameters.

The harvesting of microalgae by membrane filtration is still under development.

4. Membrane technologies for fermentation

Every generation bioethanol will go through the process of saccharification and fermentation. However, for the second- and third-generation bioethanols based on biomass, the simple sugar concentration in prehydrolyzates is often low due to the different pretreatment processes and hydrolysis efficiency [48]. Moreover, pretreatment of biomass using steam explosion or dilute acid results in fermentation inhibitors that will inhibit the subsequent fermentation [49]. Low-concentration fermentable sugars in the prehydrolyzates and fermentation inhibitors lead to low ethanol concentrations, which in turn leads to high operational cost and energy consumption for subsequent purification steps. Therefore, in order to enhance the effectiveness of prehydrolyzate fermentation, the prehydrolyzate should be detoxified to remove inhibitors and concentrated to increase sugar concentration prior to being used for ethanol fermentation.

The conventional methods for sugar concentration or detoxification include evaporation, solvent extraction, overliming, activated charcoal adsorption and ion exchange. However, most of these methods have the disadvantage of adding high processing costs, complicating the lignocellulose-to-ethanol production process, generating additional waste products, requiring long processing times and/or losing sugars [50–55]. The most important point is that conventional methods cannot concentrate sugar whilst removing inhibitors. Membranes as a separation technology can solve these two issues. Furthermore, studies have demonstrated that the capital investment for the membrane process and operating costs were lower than evaporator installation [56]. The present membrane configurations applied in these aspects include membrane distillation, nanofiltration, reverse osmosis, ultrafiltration. Table 2 summarized the membrane process applied in this application.

Membrane distillation is a thermally driven process in which a microporous hydrophobic membrane acts as a physical support to separate a warm solution containing either a liquid or a gas mixture. A schematic diagram of membrane distillation is shown in Fig. 3. The different MD process configurations (direct contact, air gap and vacuum) have been used to concentrate sugar solutions and remove inhibitors. The rejection of sugar can almost achieve 100%. The flux depends on the membrane type, feed flow rate, feed temperature and initial sugar concentration [57–60]. Furthermore, the MD process can utilize low-level heat or alternative energy sources such as waste hot steam and water, geothermal or solar energy [61,62]. In our previous studies [63], we attempted to use vacuum membrane distillation (VMD) to concentrate sugar and remove inhibitors utilizing solar energy. Under the optimal conditions of a velocity of 1.0 m/s and a temperature of 65 °C, glucose rejection was 99.5% and the flux

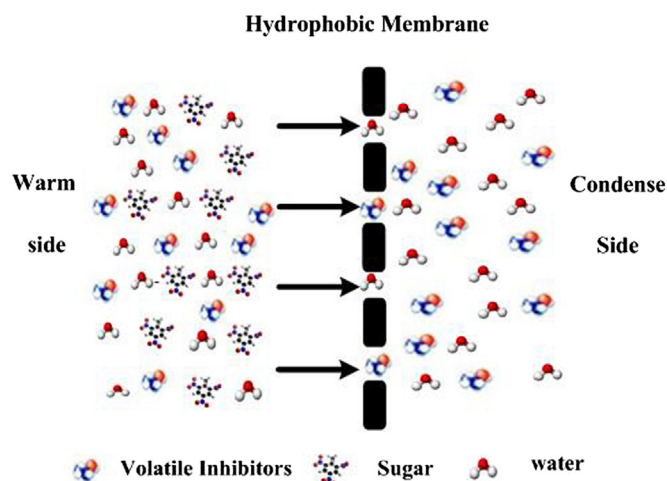


Fig. 3. Schematic of membrane distillation to concentrate sugars and remove inhibitors.

was $8.46 \text{ L m}^{-2} \text{ h}^{-1}$. Meanwhile, this process exhibited certain potential for removing inhibitors, the furfural can be removed completely.

The main disadvantages of MD are the danger of membrane wetting which can be reduced by using dilute solutions and the low removal efficiencies for some inhibitors. These disadvantages limit the industrialization of MD.

Nanofiltration has drawn great interest in biorefineries due to its low energy consumption and unique separation properties. Nanofiltration has a molecular weight cutoff (MWCO) between 200 and 1000 g/mol, allowing the retention of soluble compounds with molecular weights up to 150–250 g/mol and divalent ions [64]. The main compounds in the lignocellulosic ethanol fermentation broth include monosaccharides, aliphatic acids, furan derivatives and phenolic compounds. The molecular weight of inhibitors is between 40 and 120 g/mol, while that of monosaccharides is more than 150 g/mol. Therefore, nanofiltration can remove inhibitors from the broth and retain the sugars to concentrate the sugar solution.

Liu et al. [65] applied NF membranes with a molecular weight cut-off of 100 g/mol for the purification of hydrolyzates from the hot-water extraction of woody biomass and found that acetic acid, methanol, furfural, hydroxymethylfurfural and formic acid could all be preferentially removed from the sugar stream. The rejection efficiency of sugar was about 0.993. Han and Cheryan [64] investigated the recycling of glucose and processing of acetate from a fermentation broth by NF. They found that the separation factor of acetate over glucose in calcium magnesium acetate broth was approximately 40 using a NTR 729 NF membrane. Murthy et al. [56] reported an increase in the concentration of xylose from 2% to 10% in the reaction liquor produced by dilute acid hydrolysis of rice husk using NF. Operational costs were reduced by greater than 75%. Sjöman et al. [66] investigated the separation of xylose from glucose in hemicellulose hydrolyte using Desal-5 DK, Desal-5 DL and NF270 membranes. They reported that the separation factors of xylose over glucose ranged from 1.5 to 3.8, despite the small molecular mass differences between xylose (150 g/mol) and glucose (180 g/mol).

In theory, NF can remove all inhibitors and completely retain sugars. However, the rejection of solutes is significantly influenced by the operating conditions, such as feed concentration, feed pH, solute concentration, pressure and temperature [64,67,68]. Especially pH has an important effect on separating sugar and acids. For sugars, the retention decrease for uncharged solutes by NF was

due to the increased molecular weight cut-off, resulting from the greater intramembrane electrostatic repulsion at negatively charged state in higher pH value [67,69–71]. The rejection of acid will increase with the pH increasing. For instance, Weng et al. [51,71] used Desal-5 DK NF membranes to separate acetic acid from xylose. They found that there was a tremendous increase in acetic acid retention with increasing pH values. For example, at 24.5 bar, acetic acid retention increased from –3% at pH 2.9 to more than 90% at pH 9.1. This is consistent with the studies by Han and Cheryan [68] who reported a 60% increase in acetic acid retention when the pH was raised from 2.7 to 6.8 with an NTR729 NF membrane. Choi et al. [72] also reported a significant influence of pH level on the retention of various organic acids during NF. This occurs due to the Donnan effect coming from the electrical interactions between charged ions and membrane, which limits the transport of ions [73]. Therefore, it is a critical step to control pH in order to obtain high performance for retaining negatively charged ions.

Reverse osmosis also had attracted great attention for their unique ability to separate and purify process streams. Applications of reverse osmosis for sugar concentration and inhibitors separation from lignocelluloses hydrolyzates were studied in recent years. As the inhibitor with the highest content in hydrolyzates, a lot of works focus on removal acetic acid from hydrolyzates [68,74–76]. Acetic acid was firstly separated by Han et al. [68] from an acetic acid–glucose model solution by using RO membranes, and acetate rejection of 40% and glucose rejection of 99% were obtained, respectively. Meanwhile, RO has applied in removing other inhibitors. Sagehashi et al. [77] employed RO membranes to separate phenols and furfural from the aqueous solution derived from the superheated steam pyrolysis of biomass, and the solution was concentrated effectively by reverse osmosis separation. Several researchers also reported the separation of carboxylic acids or furans from sugars in dilute-acid hydrolyzates or fast pyrolysis bio-oils by using RO membranes [78,79]. Similarly to NF, size exclusion and the Donnan effect are two main mechanisms for molecular separation [80]. Therefore, the rejection of solutes is influenced by the operating conditions, such as feed pH, solute concentration, pressure and temperature. Different from NF, the separation mechanism of RO includes solution–diffusion. The rejection of monosaccharide retention seems independent of the feed pH values and the operation temperature. For the uncharged molecules, the dominating factors of retention were the solution–diffusion mechanism that is the major separation mechanism in nonporous, dense polyamide layer of reverse osmosis membranes [74]. Therefore, although NF was concluded as the standard membrane process for sugar concentration and inhibitors separation from lignocelluloses hydrolyzates in previous study, Zhou et al. [76] compared the NF and RO membranes performances on separating acetic acid from model hydrolyzates solution in a comprehensive way. The results showed that RO membranes are much more effective than NF membranes for retaining monosaccharides and decrease the concentration of acetic acid. It can be predicted that RO will play an important role in such application.

On the other hand, there are a lot of microorganisms and other value-added chemicals such as cellulase in an enzymatic hydrolyzate which should be recycled to improve the economic viability of the enzymatic hydrolysis of biomass. This issue can be tackled by ultrafiltration technology. Table 3 summarizes the ultrafiltration applied in recovery cellulase and other value production. The results demonstrated that the UF membranes showed almost 100% rejection of cellulases as no enzyme was detected in the permeate in several cases [81–84]. Meanwhile the UF membranes also exhibited good performance for enzyme activity recovery. UF was applied in recovering other value chemicals and obtained good performance. For instance, Chaiklahan [85] used PES membrane

Table 3

Summary of ultrafiltration applied in enzyme and other value production recovery.

Type of recovery material	Membrane material ^a	MWCO (kDa)	Membrane configuration	Membrane flux (L m ⁻² h ⁻¹)	Rejection (%)	Recovery of enzyme activity (%)	Reference
Cellulase "Onozuka" R-10	RC	10	Fat sheet	–	100	42	[82]
NOVO Celluclast L	PS	10	Fat sheet	–	–	–	[88,89]
NOVO A/S	–	10	–	–	High	69/99.5	[79]
Cellulase plus β -glucosidase	–	10	–	–	–	20.1/41	[90]
ABS cellulase	PS/PES	10,30,100/30,50	Fat sheet	–53–/49,64	98,95,60/98,94	–	[84]
Cellulase enzyme	PES	50	Fat sheet	30–1200	100	–	[81]
Celluclast plus Novozym 188	PES	5	Fat sheet	–	–	39.3/17.9	[91]
Cellulase plus cellobiase	PES	10	Fat sheet	–	–	60–66.6/76.4–88	[92]
Cellulas	PES	5,10,30	–	26.5	89.4/73.9/79.7	–	
Protein	RC	5100	–	31/44	80	–	[93]
Protein	PES	5100	–	29/41	80	–	[93]
Phycocyanin	Modified PES	50,70,100	–	50–75,75–110	99,97.5,94.2	–	[85]
Surfactin	RC/PES	30	–	10–40/30–130	90/96	–	[94]

^a RC=regenerated cellulose, PS=polysulfone, PES=polyethersulfone.

with MWCO at 50 kDa, 69 kPa to retain phycocyanin. A retention rate of 99% was found to be optimal and food grade phycocyanin with the purity around 1.0 containing c-phycocyanin as the major component was obtained.

In order to improve the recovery efficiency, Qi et al. [86] first proposed combined technology. Studies have shown [87] that, in the UF stage, the cellulase in the hydrolyzate suspension was recovered in the retentate and could be used for a subsequent round of hydrolysis of the cellulosic substrate. Glucose was completely transmitted through the UF membrane and could be collected in the permeate, which could be further concentrated by NF to increase the glucose concentration. In the NF stage, when the ultrafiltered hydrolyzate was treated by NF270 at 13.1 l/m² h, the glucose concentration increased to 110.2 g/l from 30.2 g/l, while the permeate could be collected for water reuse and recycling.

5. Membrane technology for ethanol recovery

For typical corn-to-ethanol processes, the final fermentor contains ethanol over 10 wt%. However, the microorganisms used for fermentation can tolerate a maximum concentration of bioethanol of 10 wt%. Therefore, the ethanol must be removed for continuous production. On other hand, bioethanol from cellulosic biomass likely provides lower product concentrations (<5 wt%) than bioethanol from corn. To save energy and costs, the ethanol should be concentrated before the next refining process. The conventional method to remove and concentrate ethanol is distillation. Unfortunately, this is also the aspect of distillation which is not attractive, as reported by Leland [95]

- (1) The energy requirement is significantly higher at low alcohol feed concentrations (<4 wt%) compared to higher concentrations [96].
- (2) At 101.3 kPa, ethanol–water forms an azeotrope at 95.6 wt% ethanol. Higher concentrations of ethanol cannot be obtained through simple distillation.
- (3) The process operates at high temperatures (unless under vacuum), much higher than typical optimum fermentor temperatures and usually at temperatures lethal to microorganisms, which causes the deactivation of proteins and enzymes and prevents the reuse of salts and microorganisms [97].

Thereby, opening the door to other technologies based on membranes which can save energy and cost in ethanol production is a good choice, such as reverse osmosis, ultrafiltration [98],

membrane distillation [99–106], pervaporation [107–109] and the pervaporation–distillation hybrid process [110–113].

5.1. Membrane distillation for ethanol recovery

Considering that partial pressure of ethanol is higher than that of water, ethanol vapor can transfer preferentially through the membrane pores. Meanwhile based on the mechanism of membrane distillation, it can be used to separate ethanol and water. The selectivity is determined by ethanol volatility [114]. Franken et al. [115] first confirmed the possible use of direct contact tubular membrane distillation module for separating ethanol from ethanol–water mixture. There are very few studies about separating simple ethanol–water solution using membrane distillation [115,116]. Membrane distillation for ethanol recovery focuses on coupled with fermentation and results showed that the ethanol productivity improved due to the inhibitors was removed. Direct membrane distillation and air gap membrane distillation coupled with fermentation are common configuration for ethanol production. Udriot et al. [100] integrated direct membrane distillation with fermentation for the separation of ethanol from the culture medium. The results showed 87% increase in ethanol productivity from 0.99 to 1.85 g L⁻¹ h⁻¹. Tomaszewska et al. [117] showed that the production rate was in the range of 2.5–4 g dm⁻³ h⁻¹ in the case of fermentation combined with the MD whereas in the classical batch fermentation from saccharose this rate was lower and amounted to 0.8–2 g dm⁻³ h⁻¹. Lewandowicz et al. [104] reported that ethanol production increased by 15.5% due to facilitation of the continuous process, more complete fermentation of sugars, lowering the osmotic pressure in the fermentation broth, decreasing glycerol synthesis level and increasing yeast cells number and viability. In addition to improve the ethanol productivity, membrane performance is another research focus. Studies indicate that the temperature has an important influence on membrane flux [101,104,105]. The membrane flux increases as the feed temperature increases due to membrane swell. It was found that there was no clear influence of the feed temperature on the separation factor. García-Payo et al. [101] investigated the effect of operating parameter on membrane performance for the air gap membrane distillation. Although membrane distillation for ethanol production can overcome the disadvantages of conventional batch production. Current studies have been confined to lab-scale, and larger scale performance needs to be further investigated. Moreover the membrane selectivity is relative low (1–7), developing high performance membrane material is another focus for membrane distillation.

Table 4

Summary of membranes used for ethanol recovery.

Membrane type ^a Organic			Flux (g m ⁻² h ⁻¹)	Selectivity α	Advantages	Disadvantages	Reference	
Silicon -containing polymer	Unmodified PDMS		1–1000	1–10.8	Relative cheap Easily prepared	Poor film-forming ability; relatively low permselectivity; poor mechanical properties; considerable swelling	[128–130]	
	Modified PDMS	Cross-link	Vinyl-PDMS	850	8.0	Improved Mechanical properties and film-forming ability	The flux and selectivity cannot increase simultaneously	[131]
			Acetoxysilyl-PDMS	251	10.8			[132]
		Graft	PDMS-g-PVDF	1300	5.1			[133]
			PDMS-g-PPP	19	40			[134]
		Block	PDMS/PS/PHS	4500	6.8	[135]		
		IPN ^b		160	5.5	[136]		
			–	9	[137]			
		PDMS-polyetherimide hollow fiber		231–252	7–9	[138]		
		POMS		380	5	–	–	[139]
	PTMSP		340–440	9–26	Selectivity is relatively higher	Tendency to physical and/or chemical aging Performance depends on polymerization conditions	[140–142]	
Fluoro – containing polymer	Plasma-polymerized PFP		500	10	Selectivity is relatively higher High flux	High cost; low permeability	[143]	
	Styrene-fluoroalkyl acrylate graft copolymers PVDF hollow fiber		5	45.9			[130,144]	
Other polymer			3500–8800	5–8			[98,145]	
	poly(ether block amide)		118	2.5		Low selectivity	[146]	
	PDMS-imide	560	10.6				[147]	
Inorganic	Liquid membrane (LM) TOA-LM	–	80			Low permeability Easy liquid loss	[148]	
	Zeolite		100	11.5	High ethanol selectivity; High chemical resistance, thermal	About 10–50 times more expensive than the equivalent polymeric ones Defect-free commercial-scale inorganic membranes are difficult to manufacture	[149]	
	ZSM-5		223	47			[150]	
Mixed matrix membrane	Silicalite-1		220–2550	64–218	Stability		[130]	
	zeolite		51	16.5	Combine the advantages of inorganic and organic membrane	Poor incompatibility Poor dispersion of particles in polymer	[151]	
	Silicalite-1		150	16.5–59			[152–154]	
	Polyphosphazene nanotubes		119	10			[155]	
	Carbon black		–	9			[156]	
	Fumed silica		–	7.0	[157]			

^a PDMS=polydimethylsiloxane, PVDF=polyvinylidene fluoride, PPP=poly(1-phenyl-1-propyne), PS=polystyrene, POMS=polyoctylmethyl siloxane, PTMSP=poly(1-trimethylsilyl-1-propyne), PFP=perfluoropropane.^b IPN=interpenetrating polymer networks.

5.2. Pervaporation for ethanol recovery

As opposed to membrane distillation, pervaporation systems are available for commercial applications in the removing of water from concentrated alcohol solutions. Furthermore, a lot of work has been reported about membrane materials and process [11,118–125]. However, pervaporation for ethanol recovery is at pilot stage. Considering that knowledge of dehydration by pervaporation is relatively mature, the potential for using pervaporation for ethanol recovery from dilute fermentation broth will be reviewed in this section.

Pervaporation is a method for the separation of mixtures of liquids by partial vaporization through a non-porous membrane. The separation mechanism is a solution–diffusion model. For ethanol recovery, the control process is the solution since the kinetic diameter of ethanol (0.57 nm) is larger than that of water (0.32 nm). Therefore, choosing the proper membrane material for the separation system is very important.

5.2.1. Membrane material for ethanol recovery from broth by pervaporation

According to the pervaporation mechanism, hydrophobic membranes can be used that will leave water in the retentate whilst allowing ethanol to pass through. There are two main classes into which most pervaporation membranes can be placed: polymeric membranes and inorganic membranes. Polymeric membranes are widely used today in ethanol recovery. Inorganic membranes, fabricated from zeolites and silicalite-1, have increasingly become a focus of research. A third class of membranes is commonly termed mixed matrix membranes. The membrane materials that can be used for ethanol recovery have been reported by Peng and Zhan [126,127]. The performance comparison of different membrane materials is summarized in Table 4 according to the factors (flux and selectivity) that characterize pervaporation performance. A comprehensive analysis of the pervaporation performance of polydimethylsiloxane (PDMS) shows that it is superior to the other membrane materials. PDMS will, at least in the near term, continue to be the dominant organic membrane material used for the recovery of ethanol from water.

According to the analysis of O'Brien et al. [158], a couple of systems would be cost-competitive if the performance of the pervaporation membranes could be modestly improved so as to exhibit a flux of $150 \text{ g m}^{-2} \text{ h}^{-1}$ and a separation factor of 10.3 for ethanol to water. As can be seen in Table 4, most of the membranes can meet this requirement. However, from the analysis of energy consumption, a separation factor of a membrane greater than at least 20 is needed [159]. This is the main reason for why polymeric membranes remain unindustrialized. Although the separation factor of organic membranes is over 20 and these offer a number of advantages over polymeric membranes, such as solvent resistance and the ability to operate at higher temperatures, these are more difficult to produce on a large scale industrially and are often expensive. In addition, another reason for continued disuse is performance degradation within the actual separation system [160]. This performance degradation is mainly caused by complex components in the fermentation broth. The influence of fermentation components on membrane performance during pervaporation has been investigated by several authors [161–166]. Despite this, sometimes contradictory results have been found between different studies and concrete explanations for the observed behavior re-missing. However, it is clear that membrane performance can be significantly affected by the presence of fermentation by-products, even in small amounts, which limits the commercial applicability of a pervaporation system. Therefore, exploiting and designing higher performance, reliable

membrane materials are essential for pervaporation applications in the recovery of ethanol from broth.

5.2.2. Hybrid pervaporation and fermentation process for improving ethanol yields

Continuous fermentation is more attractive than the batch process owing to its higher productivity, better process control and improved yields. However, traditional continuous fermentation has the inherent limitations of cell wash-out and product inhibition, which seriously affect the productivity of the process. One way to improve the productivity of such product-inhibited fermentations is continuous in situ removal of ethanol. Compared with traditional techniques such as gas stripping and adsorption, pervaporation is simple, highly selective and non-toxic to fermentative microorganisms. It is also potentially cheaper than distillation. Therefore, hybrid membrane pervaporation with fermentation is regarded as a promising technology [167–170].

For the technical application of the hybrid pervaporation–bioreactor process, two coupling modes have been designed. In the first, pervaporation is performed externally, while in the second, the pervaporation unit is directly integrated into the reactor. A schematic of the two coupling mode is shown in Fig. 4. Lipnizki et al. [171] discussed the advantages and disadvantages of these arrangements, and suggested the use of an external pervaporation unit due to its high efficiency and easy maintenance. Table 5 gives an overview of studies on the hybrid fermentation and pervaporation process. Obviously, ethanol productivity has been improved by utilizing a hybrid fermentation–pervaporation process compared with batch fermentation.

Meanwhile, several studies have focused on the economic assessment of the hybrid fermentation–pervaporation process for bioethanol production in terms of the investment and production cost. Most studies have come to a positive conclusion regarding the economic potential of hybrid pervaporation–bioreactor processes for high ethanol productivity and low energy consumption. However, these reports have demonstrated that the total ethanol production cost of the hybrid fermentation–pervaporation process was slightly higher than conventional continuous fermentation due to the relatively high cost of the pervaporation unit [158,172–174].

Luccio et al. [175] investigated the effect of membrane costs on the process economics of ethanol and fructose production by selective hybrid fermentation and pervaporation. For a complete plant installation, the highest allowable membrane cost to maintain economic feasibility was around $\$500/\text{m}^2$, while the adaptation of an existing plant allowed for a cost of up to $\$800/\text{m}^2$, considering a minimum return rate of return on the investment of 17%. Improving the performance of the membrane is a crucial step to reduce production costs. Wasewar et al. [176] investigated the

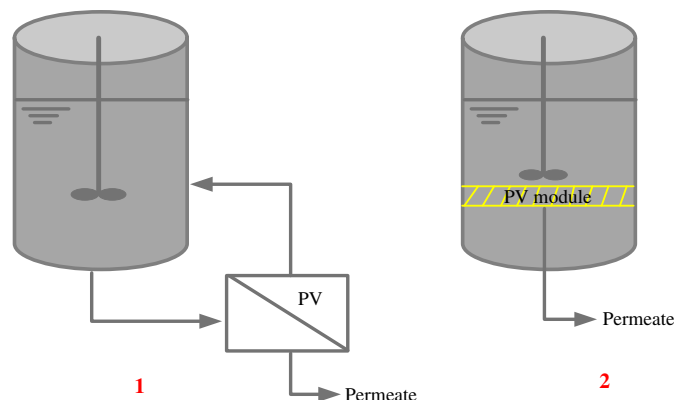


Fig. 4. Configuration of the hybrid fermentation and pervaporation process with (1) an external pervaporation unit and (2) an internal pervaporation unit.

Table 5

An overview of studies about the fermentation and pervaporation hybrid process from the literature.

Feed	Micro-organisms	Couple mode	Membranes membrane modules ^a	Flux (kg m ⁻² h ⁻¹)	Separation factor	Ethanol productivity without PV (g L ⁻¹ h ⁻¹)	Ethanol productivity coupled with PV (g L ⁻¹ h ⁻¹)	Reference
Glucose	Baker's yeast	External	PDMS/PP or PTFE tubular	3.96	5.8–9.0	1.6	6.3 (+293.75%)	[179]
Dextrose	<i>Saccharomyces cerevisiae</i>	External	PDMS/PS, tubular	0.56	5	10	30 (+200%)	[180]
Glucose	Baker's yeast	External	PDMS/PS hollow fiber	0.39–0.81	2.5–5.7	4.5	8.8 (95.6%)	[177]
Lactose	<i>Saccharomyces cerevisiae</i>	External	PDMS coated on PS tubular	0.05–0.18	4–12	1.2	15 (+25%)	[181]
Glucose	<i>Saccharomyces cerevisiae</i>	External	LTV SR/PS flat sheet	1.2	5.5	1.74/1.76	2.75/3.25 (84.6%)	[182]
Glucose	<i>Saccharomyces cerevisiae</i> ATCC 4126	External	PDMS/PS flat sheet	0.25–0.63	1.8–6.5	2.92	4.9–7.8 (67.8–167%)	[183]
Glucose	<i>Saccharomyces cerevisiae</i>	External	Composite PDMS flat sheet	0.135/0.091	7.7/8.2	0.54/0.52	≥ 0.23/ ≥ 0.38	[184]
Lactose	<i>Saccharomyces cerevisiae</i> B4	External	PDMS–PAN	2.6–3.5	> 8	–	0.9	[185]
Glucose	yeast	External	PDMS/PA flat sheet	0.3–0.69	5.0–7.2	3.21	9.6 (199%)	[186]
Glucose	yeast	External	PDMS/PA flat sheet	0.774	4.85	0.7	1.39 (98.57%)	[187]

^a PDMS = polydimethylsiloxane, PP = poly(1-phenyl-1-propyne), PTFE = polytetrafluoroethylene, LTV SR = LTV silicone rubber, PS = polysulphone, PAN = polyacrylonitrile, PA = polyamide.

effect of membrane flux and selectivity on the ethanol production cost. A 22% reduction in the direct production cost of ethanol was found when the flux was increased by 200%. A 10% decrease in the direct production cost of ethanol was observed when the separation factor increased by 20% and costs decreased by 35% for a 100% increase in the separation factor. Therefore, developing higher performance and more reliable membranes will significantly reduce the ethanol production cost.

During the hybrid process, cells and other by-products will lead to membrane fouling. To reduce the effect of fouling, microfiltration can be used to retain the remains of cells in the fermentation broth. In addition, Groot et al. [177,178] compared the different process alternatives and concluded that continuous ethanol production with recycling of the microorganism using microfiltration leads to the lowest production costs. The costs were 15% lower in comparison to the batch process.

In summary, the hybrid fermentation and pervaporation process will have good potential in ethanol production with the development of a high performance membrane. Meanwhile, further studies should focus on optimizing hybrid process integration with UF to enhance the ethanol productivity and reduce costs.

6. Conclusions

Membrane processes exhibit great potential and show suitable performance in the bioethanol production. For microalgae harvesting, more than 90% microalgae can be retained by the micro- and ultrafiltration process. Especially, hydrophilic organic and inorganic ultrafiltration membranes show high recovery efficiency. The existing problem of this technology is membrane fouling which can be controlled by selecting the appropriate membrane material and operational model. Nanofiltration, membrane distillation and reverse osmosis can remove inhibitors and concentrate sugars. Nanofiltration and reverse osmosis exhibits great potential due to its low cost and high efficiency; moreover, it can be coupled with UF to recover other value-added chemicals such as cellulase in the enzymatic hydrolyzate. Although membrane distillation can separate ethanol from water, the separation factor is relatively low. Pervaporation is the preferred technology for ethanol recovery, but developing a good performance membrane material for practical applications is a problem urgently to be

solved. A hybrid fermentation and pervaporation process would be advantageous in ethanol production with the development of an adequately performing membrane. We thought that further studies should focus on optimizing the hybrid process by integration with UF to enhance ethanol productivity and reduce the cost, and a particular challenge to research in this field is the transition from pilot studies to industrial operations.

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